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Safety Issues for Hydrogen-Powered Vehicles

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SAFETY ISSUES FOR HYDROGEN-POWERED VEHICLES

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ABSTRACT

This paper reviews how the basic properties of hydrogen and the history of hydrogen handling can contribute to understanding what system design and operational features must be in place to maximize safety for these vehicles. The history comes from several sources: discussion with a commercial hydrogen supplier, hazard analysis drawn from industrial and NASA experience, and reports published by groups fielding demonstration hydrogen powered vehicles. There is abundant evidence that hydrogen can be handled safely, if its unique properties — sometimes better, sometimes worse, and sometimes just different from other fuels — are respected. Two critical issues are hydrogen leak prevention and detection in otherwise normal operating circumstances and the safe venting of hydrogen to avoid excessive pressure build up in storage. This is largely an issue of good engineering and appropriate materials selection. Flammable or detonable fuel-air mixtures in confined areas must be avoided. Refueling and maintenance also raise issues. Here, adherence to safe operating procedures that keep hydrogen and air separate are critical. Crashworthiness and the allowance for safe emergency venting of hydrogen after an accident are issues too, but these should not overshadow the normal operations issues.

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SAFETY ISSUES FOR HYDROGEN-POWERED VEHICLES

Introduction and Summary of Conclusions

California's upcoming very low and zero emission vehicle standards have spurred research in new automotive technologies. At Sandia, we are applying our experience in hydrogen technology to vehicles powered by hydrogen internal combustion engines, which can fall into the very low emission category, and electric vehicles powered by hydrogen fuel cells, which produce no pollutants at the vehicle. This research and development work builds on our capabilities in combustion research and in materials for hydrogen storage and handling.

Any discussion of hydrogen fuels immediately opens a question of safety. Many people, including this author before beginning this review, think first about the Hindenberg fire in 1937. The fundamental concerns in dealing with hydrogen are indeed the potential for fire and, in enclosed areas, for explosion. However, in the two generations since the Hindenberg, hydrogen has become widely and routinely used in a variety of industrial processes. While most is generated and used at the same facility or within pipeline distance, on the order of a hundred million gallons of cryogenic liquid hydrogen are transported on North American highways each year.

This paper reviews safety issues and experience that might be applicable to hydrogen-powered vehicles. The report concentrates on issues associated with the vehicle itself: refueling, on-board fuel storage, and operation. The discussion will be applicable both to fuel cell and to internal combustion vehicles. Some issues are specific to the type of on-board hydrogen storage. Three modes have received most of the attention: compressed gas, cryogenic liquid, and metal hydrides. (Metal hydride systems bind hydrogen to various metals, including iron, magnesium, nickel, manganese and titanium, that release gas when the hydride is heated.) More recently, media such as finely divided activated carbon, which adsorbs hydrogen onto its surface, have been proposed. Hydrogen is adsorbed and stored at cryogenic temperatures (but well above hydrogen's boiling point), and released as the media is heated.

Safety information has been drawn from a variety of sources. Quantitative risk results from these other applications may not be directly applicable to hydrogen-powered vehicles, but hazard and issue analyses do carry over.

A great deal was published on hydrogen safety in the 1970's and early 1980's because of the interest in alternative energy sources and the hydrogen economy. Some, but less, has been published since. There have been several discussions in the literature on hydrogen's physical properties and their implications for safe hydrogen handling. These are often coupled with comparisons between hydrogen and other fuels. What is somewhat harder to find are records of real experience. In the 1970's, Factory Mutual Research Corporation and NASA each published incident data summaries. Although not current, these provide an excellent picture of what can happen when handling hydrogen. Hydrogen-powered vehicle demonstration projects have been going on since the mid-70's although the number of vehicles on the road has been very small. Reviews of hydrogen vehicle technology and safety issues have been recently published by De Lucci [Ref. 1] and Hansel, et al. [Ref. 2].

Relatively little information about commercial hydrogen transportation has been published recently. It is now a reasonably mature industry going about its routine business. To get a picture of current liquid hydrogen transportation safety issues, the author has had several conversations with James Hansel, of Air Products and Chemical, Inc. Air Products is the largest, but not the only supplier of commercially delivered liquid hydrogen.

This paper does not attempt to answer the question, "Will hydrogen-powered vehicles be safe?" Their safety will have be clearly demonstrated before they leave the laboratory and are widely accepted. Quantitative safety studies specific to hydrogen-powered vehicles will be a part of that. The better question to work towards now is, "What system design and operational features must be in place (and at what cost in money and convenience) to assure this safety?" While prescribing design choices now is still premature, we can draw several top-level conclusions.

- *There is abundant evidence that hydrogen can be handled safely, if its unique properties -- sometimes better, sometimes worse, and sometimes just different from other fuels -- are respected.* The safety record in commercial hydrogen transportation is excellent. This record is grounded in a respect for hydrogen's properties. It can be better than other fuels: in open air settings its extreme buoyancy and high rate of diffusion allow for very rapid dispersal. It can be worse: hydrogen/air mixtures in enclosed areas are more likely to detonate than most fuel/air mixtures. And it can be just different: its clean, almost invisible, and relatively cool flame is very unlike a gasoline flame.

- *The most critical safety design issue for hydrogen-powered vehicles is leak prevention and detection in otherwise normal operating circumstances.* Hydrogen's fundamental properties suggest leakage from storage vessels and transport lines during normal operations may be an issue. Experience in industry, at NASA, and in transportation confirms this.

- *Materials for hydrogen storage must be selected appropriately.* Much of the experience with leakage can be traced to materials issues. Common high strength steels should be avoided because of the potential for embrittlement. Depending on the application, appropriate materials may include some lower-strength steels, high strength stainless steels, aluminum, or plastic lined fiber composites. Experience on the latter two, while promising, is incomplete. Features such as metal-to-metal joints and packless valves are preferred to avoid small leaks.

- *Hydrogen should be used in well-ventilated areas if at all possible.* This avoids the explosion hazard if leakage does occur. Outdoor operations are best. If operations are indoors, areas should be well ventilated. On vehicles, points such as joints that are prone to leakage should be in relatively well-ventilated locations.

- *Provision must be made for the safe venting of hydrogen to avoid excessive pressure build up in storage.* This is important in any type of pressurized storage system, but is especially an issue for vehicles using liquid hydrogen where boil-off is unavoidable. Some sort of internal gas capture and utilization may be possible. If gas must be released, gas should be vented into areas where hydrogen will disperse rapidly (i.e., not into an enclosed garage) and away from potential ignition sources. Vent stacks themselves must be carefully designed. The challenge is to find the least obtrusive combination of design features and operational constraints to maximize safety.

- *Care must be taken to purge air from hydrogen storage vessels and delivery lines (and vice versa) during vehicle refueling and maintenance.* Purging problems have been at the root of many industrial and NASA incidents. In a vehicle context, during refueling, care is needed to purge air out of hydrogen tanks and filling lines. Before maintenance, purging the engine and vehicle fuel lines of hydrogen becomes the issue. Afterward, air must be purged.

- *Crashworthiness is important but should not overshadow normal operations issues.* Vehicle design will have to address the obvious weight trades between crashworthiness and performance. Storage and fuel line placement must be considered, as should emergency venting of hydrogen after an accident. Fuel lines may be more fragile than storage vessels, so there should be provision for automatic excess flow shutoff if the former is damaged. While collision safety is a real and perhaps the most visible concern, it is worth reiterating that it is only one of several safety issues that need to be addressed.

The body of this paper is organized into three sections. The paper begins with a discussion of hydrogen's safety-related physical properties. Basic properties help to define what issues need to be addressed. These properties can also lead to

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fundamental design or operational limitations. However, safety depends on how effectively system implementation deals with these issues and limitations. Thus, the next part of the paper discusses hydrogen handling experiences in four areas: commercial highway transportation of liquid hydrogen, industrial applications as reported by Factory Mutual Research Corporation, NASA's experiences, and the rather limited safety history of hydrogen-powered vehicles themselves. The second and third of these also discuss some transportation incidents. All illustrate, in different contexts, how real systems address the hazards the physical properties present and where the residual issues lie. Based on all these sources, the third section outlines some of the design and operational issues hydrogen-powered vehicles will have to address. The paper concludes with some comments on what safety analysis issues might be pursued next.

1. Safety-Related Physical Properties and Issues

Any discussion of hydrogen safety must begin with the basic physical properties of hydrogen. To put information in perspective, this section presents comparable data for methane (the primary constituent of natural gas), propane, and gasoline, where available. Some properties identify specific conditions that present comparatively greater or lesser hazards for hydrogen relative to other fuels. Since safety really depends on how effectively the system design and operation deals with these conditions, however, it is premature to examine a table of properties and conclude that one fuel or the other will be more or less safe in actual application.

The fundamental safety concern lies with hydrogen's potential to ignite or explode. Section 1.1 introduces the physical conditions for the ignition of a fuel-air mixture: flammability limits, ignition energy, and autoignition temperatures. Properties and observations related to explosion and resulting overpressures are given in Section 1.2. Section 1.3 discusses properties associated with the creation (or prevention) of flammable or detonable fuel-air mixtures: storage, leakage, and subsequent dispersal of stored hydrogen. That section will discuss materials selection to avoid embrittlement of storage vessels. Following that, Section 1.4 discusses the consequences and control of a hydrogen fire compared to some of the other fuels.

Apart from flammability, cryogenic liquid hydrogen presents some special issues. These are discussed in Section 1.5.

Two other potential hazards should be noted, even though they will not be developed further. First, for any pressurized gas systems, including, but not limited to hydrogen, failure of storage vessels and piping presents mechanical hazards. Second, while hydrogen gas is not toxic, if hydrogen replaces enough oxygen in an enclosed area, asphyxia can result.

1.1. Ignition Properties

Initiating a hydrogen fire takes two things: a fuel-air mixture of proper proportions and an ignition energy source of sufficient strength. Table 1 gives the fundamental properties associated with these for the various fuels. Table 1 also gives detonability limits. These will be discussed in Section 1.2.

These fundamental properties relevant only in so far that they shed light on potential hazards in real situations. There are three questions to ask.

The first question is, "When do flammable fuel-air mixtures occur?" The flammability limits in Table 1 give the bounds on concentrations for various fuels. Hydrogen has the widest range between upper and lower limits: any mixture between 4 and 75% by volume of hydrogen in air can be ignited. In unconfined or open-air situations, only the lower limits tend to be important. Here, methane and hydrogen are comparable while gasoline and propane have smaller lower limits. This does not, of course, imply that spilled methane will produce the smallest volume that contains a flammable fuel-air mixture and gasoline the largest. Fuel concentrations depend on spill size and geometry, plus the leakage and dispersal rates. The upper bound for hydrogen is much higher than for other fuels. High concentrations are a possibility in enclosed spaces, especially where no ignition sources are available to ignite a leak immediately. In this case, hydrogen may be at a comparative disadvantage. Since, as we will see in Section 1.2, high concentrations of hydrogen in enclosed areas may readily support detonation, this comparative disadvantage may be considerable.

While these *qualitative* observations are broadly supportable, one should, however, be careful not to draw *quantitative* conclusions from the data in Table 1 without a specific context. In some situations, it might be more relevant to compare fuel gas releases in terms of equal combustion energy, rather than equal volume. The volume-base numerical comparison between hydrogen gas and methane in Table 1 would need to be adjusted. When burned, hydrogen gas releases about 10,000 KJ/m^3 compared to roughly 30,000 KJ/m^3 for methane [Hord, Ref. 3]. A five-fold difference in upper volume fractions corresponds to only about a 5/3 difference on an energy basis.

A second question is, "What sources can ignite a flammable mixture?" The row in Table 1 labeled "Ignition energy" gives the energy required to ignite a stoichiometric fuel/air mixture, i.e., an ideal mixture where the proportions are such that all the oxygen in the air can combine with all the fuel with none of either remaining. All the ignition energies in Table 1 are low relative to real sources. For example, the discharge from an electrostatic charge on a person can be as high as 10 mJ — over thirty times higher than any of the minimum ignition energy values in Table 1. Open flames will ignite any fuel. The 0.02 mJ ignition energy for hydrogen is the minimum energy. If the mixture is not stoichiometric (not an ideal mixture of fuel

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and air), somewhat higher energies are required. The dependence of ignition energy on mixture for hydrogen and methane is given in Figure 1. At the lower fuel concentrations, which, as noted before, are applicable in open-air settings, methane and hydrogen are quite comparable. Even so, there are situations where hydrogen's very low ignition energies do have practical import. A sudden discharge through a relief valve or burst disk has, in some cases, ignited [Ref. 2]. Electrostatic ignition of gas in vent stacks has also been observed.

Table 1. Flammability, Detonability, and Ignition Properties of Fuels

Fuel	Hydrogen	Methane	Propane	Gasoline
Flammability limits				
Lower (% fuel by volume)	4.0	5.3	2.1	1.0
Upper (% fuel by volume)	75.0	15.0	10.4	7.8
Detonability limits				
Lower (% fuel by volume)	18.3	6.3	3.4	1.1
Upper (% fuel by volume)	59	13.5	see note	3.3
Ignition energy (mJ)	0.02	0.29	0.31	0.24
Thermal autoignition				
Minimum	520C	630	450	
Heated Laminar Air Jet (1 mm d)	640	1040	885	
Heated Nichrome Wire (1 mm d)	750	1220	1050	

Sources: Flammability limits, detonability limits, and ignition energy are from Karim [Ref. 4]. Many other references (e.g., Hansel et al. Ref. 2) give 74% as the upper flammability limit for hydrogen. Thermal autoignition values are from Hansel et al. [Ref. 2]. Karim is the only reference that gives detonability limits for propane and there is an obvious error in that source's report that the upper limit is 35%.

The thermal autoignition numbers in the last rows of Table 1 give the temperatures of various sources that will ignite hydrogen. These, too, require some interpretation, as is discussed in Hansel, et al. [Ref. 2]. The minimum values suggest hydrogen is less easily thermally ignitable than propane. The conditions under which this is true — "quasi-adiabatic" heating in a closed vessel — are not

necessarily representative of real situations. The values on the second and third line more closely represent real sources. For these, hydrogen's ignition temperatures are lower. Also, it should be noted that catalytic effects can reduce autoignition temperatures [Fischer, Ref. 5]. Again, the practical import of these results depends on the situation.
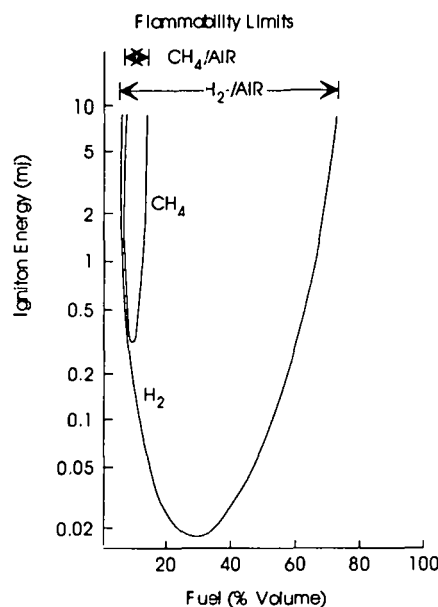
Figure 1. Ignition Energy for Hydrogen (H_2) and Methane (CH_4) as a Function of Mixture

Source: Fischer [Ref. 5].

The third and ultimate question is, of course, "Following a release, will the flammable fuel/air mixture meet an ignition source of sufficient strength?" This depends very strongly on the situation. The lower the ignition energy, the larger the number of low energy sources that can ignite the fuel and hence more likely the chance of the fuel will meet a sufficiently strong source and ignite. The size of the volume containing a flammable mixture depends the range of mixtures that support combustion, the amount of fuel released, and the rate at which fuel disperses. As will be discussed more fully in section 1.3, hydrogen disperses more quickly than other fuel gasses in unenclosed areas. In enclosed and partially enclosed areas, however, hydrogen's wide flammability range may lead to relative large volumes containing a flammable mixture. The larger the volume, the more likely the ignition.

1.2. Explosion

The ease with which a hydrogen fire in a confined area can transition to an explosion is the major issue for hydrogen safety. The resulting overpressures can do significant damage.

As described by Fischer [Ref. 5], the process leading to detonation begins when the character of the flame front changes from laminar to turbulent structures. Interactions of reflected pressure and shock waves with the flame front, plus pressure preheating of the unburned gas mixture, can accelerate flame speeds. This deflagration can build to a detonation shock wave propagating with supersonic speed relative to the unburned gas mixture. The temperature rise with compression in the shock wave autoignites the fuel-air mixture.

All the gaseous fuels can support detonation. However, the burning velocity for hydrogen is much higher than the other fuels: up to 346 cm/sec (depending on the mixture) versus values between 35 and 50 cm/sec for gasoline vapor, methane, and propane. Thus, the process is considerably more likely in a hydrogen mixture. Whether detonation actually happens depends strongly on the geometry and the strength of the initial ignition source. Table 1 gives the limits on the fuel-air mixtures that can support a detonation. Except in some very special circumstances, with very strong ignition sources, detonation requires the fuel-air mixture be in an enclosed volume. (Burning velocities appear in references 3, 4, 5, and 6. The value for hydrogen comes from Fischer [Ref. 5] which is higher than that stated elsewhere. Fischer discusses detonation phenomena in detail, so this may reflect more recent work.)

The overpressure that results from a deflagration or detonation presents both a direct hazard and a secondary shrapnel hazard. The actual overpressures and hazards depend on the degree of confinement and the geometry. Fischer [Ref. 5] reports that deflagrations of stoichiometric mixtures of any of the gasses in a confined, unvented spherical or cubical volume can produce 8:1 pressure rises and detonations can show about 20:1 or more.

Reider and Edeskuty [Ref. 7] report on three less controlled hydrogen deflagration and detonation incidents that illustrate the difference confinement can make on the resulting overpressure. In the first, about 200 pounds of hydrogen gas exploded during an outdoor experiment. In this totally unconfined case, an overpressure of about 0.5 psi was observed 150 feet from the blast. A nearby lightly metal clad building suffered some denting and broken windows. Some doors were opened by the following negative pressure phase. In the second example, 30-50 pounds of hydrogen gas exploded inside a light sheet metal shed. This lightly confined explosion produced what was estimated to be between 25 and 30 psi. This undressed some of the sheet metal walls from the frame of the shed. Among the thirteen people in and near the shed, there were bruises, ruptured eardrums, and, in

one case, a fractured heel. The final example was one of a series of detonation tests in a heavily confined blockhouse. The greatest overpressures seen were about 200 psi. This was about a 13:1 rise above atmospheric pressure. Only about 6 pounds of hydrogen was involved in this test, but it was in a near-stoichiometric mixture.

1.3. Properties Related to Storage, Leakage and Dispersal.

In a vehicle application, hydrogen could be stored as a gas in a pressure vessel, as a cryogenic liquid in a dewar, or as a hydride. Fuel lines from the storage tank to the engine would carry gaseous hydrogen under pressure. Under normal conditions, this storage and fuel delivery system would keep hydrogen and air separate so as to avoid flammable or detonable mixtures. Several properties of hydrogen must be considered in maintaining an intact and leak-free hydrogen storage and delivery system.

One of the fundamental issues for storage systems is hydrogen embrittlement. Hydrogen stored under even low pressures can permeate metals and in some cases greatly reduce their fracture toughness. Small flaws and cracks can grow slowly and lead to delayed but catastrophic failure. Embrittlement-caused failure depends on the material used, the pressure at which the hydrogen is stored, whether that pressure is constant or cycling, and the quality of the construction of the storage vessel.

Embrittlement need not be a safety issue if appropriate materials are chosen for hydrogen storage and transport, but the properties of hydrogen must be respected. Storage vessels of steel, aluminum, and polyethylene lined composites have been discussed. Oien, Spingarn, Robinson, Bartel, and Adolphson [Ref. 8] have reviewed these at some length.

Common high strength steels embrittle readily, to the point that a vessel made of a steel with a 300 Ksi yield strength may fail holding hydrogen at less than 1 psi constant pressure. Lower strength steels (50 Ksi) may be acceptable in low, constant pressure applications. A high level of quality control is needed to limit the sites at which small cracks can grow. Welds provide a common source of defects. Welds should either be avoided or made with considerable care at points where the stress on the vessel or pipe is quite low. Stainless steels are much more resistant to embrittlement.

Pure aluminum and most of the aluminum alloys are generally considered to be similar or better than stainless steels in their resistance to embrittlement, provided dry hydrogen gas is stored. (Water vapor has been shown to accelerate fatigue cracking.) This conclusion is based primarily on short and medium-term (no more than one year) exposures. Since some theoretical studies suggest a possibility for

embrittlement, perhaps with long incubation times, extended duration tests are needed to confirm any overall conclusions about storage in aluminum.

Lightweight composite vessels using a high density polyethylene liner overwrapped with carbon and glass fibers can be very strong and light. Some minor permeation of hydrogen through the type of vessel is expected. The rates are small enough not to raise any direct safety concerns. The only issue is whether the presence of molecular hydrogen in the material could cause mechanical degradation. To date, this has not been seen, although very little work has been done at high pressures.

Given that catastrophic failure of storage vessels can be avoided, leakage from joints and other small openings becomes an issue. Because of its small molecular diameter, gaseous hydrogen can leak through openings more readily than other gasses. In some cases, hydrogen can pass through tiny openings that would be tight with other gasses. Actual behavior depends on the leak, but some observations have been made in the literature.

Swain and Swain [Ref. 9] compare hydrogen with methane. Actual leakage rates depend on the type of flow, size of the opening, and the pressure differential, but relative rate comparisons between the two gasses can be made. If the leakage can be modeled as diffusion, the rate scales as the diffusion constant. The volumetric flow rate for hydrogen would be about four times higher than that for methane. If the flow is laminar, the volumetric leakage rate scales inversely as the dynamic viscosity. In this case, the flow rate for hydrogen would be 1.3 times higher than for methane. If the flow is turbulent, the rate scales inversely as the square-root of the density, so the flow rate of hydrogen would be 2.8 times higher. Swain and Swain go on to experiment with small leaks of the sort that might be found in low pressure residential gas lines. They fabricated four leaky gas line fittings to replicate typical installation errors and tested six other corroded pipe sections removed from service by the People Gas Company of Miami, Florida. In all cases, they found the laminar flow model through the leak to be appropriate. However, these may or may not be representative of vehicular applications.

Martin [Ref. 10] makes some similar observations about liquid hydrogen. Its viscosity is only about 1/12 that of liquid nitrogen and 1/5 that of liquid methane (LNG) so, assuming a laminar flow model, leakage rates would potentially be relatively high.

Hansel, et al. [Ref. 2] does not deal with leakage in as quantitative a fashion, but notes that in operational experience, metal-to-metal joints and seals (flared or compression joints) are generally acceptable. Non-metal seals (gaskets, packings, and pipe-thread compounds) are much more at risk because the hydrogen can displace the sealant.

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The same properties that allow hydrogen to permeate metals and plastics and to leak through small openings also allow it to disperse away from the leak quickly. At standard temperatures and pressures, hydrogen is extremely buoyant, so in open-air settings, hydrogen will rise relatively quickly. Hydrogen will diffuse more quickly than other gasses because of its high diffusivity. Table 2 gives diffusivity and buoyancy properties for four fuels. Note both propane and gasoline vapors are heavier than air, so they will not rise away from the spill. Gasoline, being a liquid, will pool and remains the longest.

Table 2. Buoyancy and Diffusivity Properties of Gaseous Fuels in Air at Standard Temperature and Pressure

Fuel	Buoyancy (density as a percent of air)	Diffusion Coefficient (cm/sec^2)
Hydrogen	7%	.61
Methane	55%	.16
Propane	152%	.10
Gasoline vapor	~400%	~.05

Source: These values are from Karim [Ref. 4], although these agree with one of the most quoted sources, Hord [Ref. 3], which does not give values for propane. Other sources sometimes give different diffusion coefficients. Das [Ref. 6] gives values of .63, 0.2, and .08 cm/sec^2 for hydrogen, methane, and propane, respectively. Data at 20°C, 1 atm.

These results do not directly apply to liquid hydrogen spills. Just above boiling, hydrogen gas is not lighter than air. Vapor from boiling liquid hydrogen must warm before it rises. Several sources, including Martin [Ref. 10] and Das [Ref. 6], report that 500 gallons of liquid hydrogen can dissipate to below the explosive mixture limit in about 1 minute. However, neither source references the original tests leading to this conclusion nor identifies the test conditions. Witcofski and Chirivella [Ref. 11] report on tests done by NASA where 1500 gallons of liquid hydrogen were spilled in about 35 seconds. In a 5 m/sec wind, they found the cloud of vapor dispersed to below the flammability limit in about 90 seconds. In the process, the cloud traveled 160 meters downwind and reached a height of 65 meters They found dispersion, not turbulence, was the dominant mode of dissipation.

The practical importance of these properties -- and which come into play -- depends on the situation. In vessels specifically designed for hydrogen storage with appropriate materials and fittings, occasional checks for leakage may be all that is necessary. If hydrogen is used in a less appropriate system, more regular monitoring and maintenance may be necessary. As will be seen later in this paper, hydrogen leakage has been a major issue underlying a great many incidents. If leakage occurs, mixing of air and hydrogen may be by diffusion or by turbulent mixing, depending on the situation. Outdoors, buoyancy may limit flammable hydrogen concentrations while indoors it may lead to locally high concentrations that need to be dealt with by an appropriate ventilation system. This provides one incentive for carrying out operations outdoors if possible.

1.4. Properties of Hydrogen Fires

Once ignited, hydrogen flames are almost invisible in daylight and radiate relatively little heat. Hord [Ref. 3] notes that atmospheric moisture will absorb 45% of radiant hydrogen flame energy in 8m. (This result is for air at a temperature of 25 degrees C with 15 mmHg partial water vapor pressure; saturation pressure is 24mmHg.) These properties make a hydrogen fire relatively hard to detect and avoid. These properties also mean that there is relatively less danger to nearby people and property once the fire is located.

Hydrogen fires have no soot or smoke. This is also true of methane, but not of gasoline. This too makes hydrogen fires harder to find, but there is no risk of smoke inhalation from a hydrogen fire unless other combustibles are involved.

Hydrogen fires burn very rapidly and are often short-lived. This statement sometimes appears in the literature without elaboration. Its applicability depends on the circumstances. For a relatively small leak flowing from a large source it is not applicable, but if all the hydrogen is spilled at once, combustion will be relatively rapid. Hord [Ref. 3] does a simple comparison of spilled liquid hydrogen and gasoline. On an equal-volume basis, he estimates the hydrocarbon fire would last five to ten times longer. On an equal-energy basis, the gasoline fire would last up to 3 times longer.

Fighting a longer-lived hydrogen fire is different from fighting a gasoline fire. As noted in the National Fire Protection Agency Standards 50A and 50B for Gaseous and Liquid Hydrogen Systems [Ref. 12], the primary means to extinguish a hydrogen fire is to remove the fuel source. Small fires can be fought with dry chemical, steam, or inert gas. However if the hydrogen continues to flow, the dangers of reignition with the potential for detonation are often greater than those for an otherwise stable burning leak.

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1.5. Liquid Hydrogen

Liquid hydrogen boils at -252.9 C at atmospheric pressure. In converting from a liquid to a gas at standard conditions, it expands roughly 850 times in volume. These properties have a few simple safety implications. People handling cryogenic hydrogen must be properly protected against frostbite and cold injury. Breathing cold vapor can also be a hazard. Dewars that store liquid hydrogen are not perfect insulators, so as heat enters, some liquid will boil off and the pressure will build. To avoid catastrophic failure, there must be provisions to release this pressure in a controlled way that does not present a fire or detonation hazard. This gas can either be vented to the atmosphere or destroyed in some way (small fuel cells and catalytic burners have been suggested). Long vents, where the flammable mixture is sufficiently large and confined to support detonation, may be especially at risk. In the process of venting from the storage vessel (100% hydrogen, 0% air) to the atmosphere (almost 0% hydrogen, 100% air), there will always be some volume containing intermediate flammable hydrogen/air mixtures. This flammable volume should be minimized and must be well controlled to avoid ignition sources. Venting arrangements must also take into consideration abnormal conditions such as external fires or vacuum failures in the dewar. (The also applies in compressed gas and hydride storage systems where there must be provision for relief of accidental overpressurization.) In these circumstances, the venting rates may need to be relatively fast.

1.6. Some Basic Safety Principles

From this discussion of physical properties, it is possible to draw several basic principles in dealing with hydrogen. The biggest issue associated with hydrogen handling is its potential to deflagrate or detonate when ignited in an enclosed area. Since relatively low energies can ignite a flammable mixture, the emphasis must be placed on avoiding flammable, and especially detonable, hydrogen-air mixtures in the first place. This leads to several practical principles.

Air should be purged from the hydrogen storage and delivery system. If not, flammable or detonable mixtures in the storage/delivery system may be present.

Storage and delivery systems must use appropriate materials and be of quality construction. Embrittlement can cause catastrophic failure. Stainless or low-strength steels, as well as aluminum or polyethylene-lined composites, may be appropriate, depending on the application. Quality construction is needed to minimize small cracks and defects that could grow.

Care must be taken to minimize leakage from storage systems. This is a concern with any gaseous fuel. In some cases, hydrogen will pass through small

openings more rapidly than would other gasses. Vessels and joints should be checked regularly and metal-to-metal seals and packless valves, which are less likely to leak, are preferred.

Vents, when used, must be carefully designed. Vented hydrogen must be directed away from nearby ignition sources. The unavoidable volume containing a flammable mixture should be minimized and must be well controlled to avoid ignition sources. It may be possible to avoid some routine venting by controlled or catalytic oxidation of small quantities of gas.

Operations should be outdoors as much as is feasible. This exploits hydrogen's buoyancy and rapid dispersal if there is a leak or if venting is necessary.

If operations are indoors, the areas should be well ventilated and ignition sources should be minimized, even though they probably cannot be eliminated. It may be desirable to have a high rate ventilation system actuated by a hydrogen sensor.

If hydrogen ignites, dealing with the fire presents issues that are different from, but not necessarily worse than, other fuels. The issues here are twofold:

Locating a hydrogen fire is sometimes a problem because the flame is hard to see, radiates little heat, and produces no smoke. The latter two properties make approaching a hydrogen fire to deal with it, once it is located, somewhat easier.

It is best to extinguish a hydrogen fire by removing the fuel source. Reignition may lead to a detonation that would be worse than the original fire.

And finally,

Liquid and pressurized storage devices need pressure relief devices that can deal with both normal and abnormal circumstances. Normal circumstances include pressure increases from boil-off of liquid hydrogen. Abnormal circumstances include vacuum failure in the dewar and external fires.

Cryogenic liquid hydrogen must be handled so as to avoid cold burns. Protective clothing may be needed. Cold vapors should be avoided.

These issues and associated safety principles give guidance for the handling of hydrogen. Most sound fairly obvious; none sound especially onerous. It is necessary to review in-the-field experience to understand which of these have proven easiest and most difficult to manage in practice.

2. Hydrogen Handling Safety Experiences

Hydrogen is used in several ways today. The largest usages are in ammonia production and in the refining of petroleum, but there are several other applications ranging from metal processing to rocket propulsion. Most of this hydrogen is produced by steam reforming of natural gas. Most is generated at the plant where it is used or within pipeline distance. However, commercial hydrogen suppliers serve some of the smaller users for whom it is not worthwhile to invest in on-site production and act as a back-up for the larger users. The following sections review some of this experience in the four areas: commercial hydrogen transportation, industrial application, NASA operations, and the few hydrogen-powered vehicle demonstrations.

2.1. Commercial Hydrogen Transportation

The experiences in this industry are quite relevant to hydrogen-powered vehicles. Some liquid hydrogen storage issues are shared by commercial tankers and hydrogen vehicles using liquid storage. Loading and unloading a tanker is analogous to vehicle refueling. Both face road accident environments, although the response of a large truck will not be identical to that of a smaller vehicle.

This section reviews how the industry manages safety and industry's recent safety record. The overall record is excellent. The few incidents that have occurred do point to the sorts of things that can happen. Some older transportation safety information from other sources is discussed in Sections 2.2 and 2.3. The information in this section comes from two published discussions of the liquid hydrogen transportation industry: McHugh [Ref. 13] and Martin [Ref. 10]. At the time of these articles, McHugh was with Air Products and Chemicals, Inc. and Martin was with the Linde Division of Union Carbide. These companies are the largest suppliers of commercial hydrogen. Much in this section, including the safety incident data, comes from personal communications with James Hansel of Air Products [Ref. 14].

Only about 1% of the hydrogen used is supplied by commercial suppliers, mostly by truck trailers carrying liquid hydrogen. (There is also some barge traffic and some gaseous hydrogen delivery.) Still, the quantities are not small. At Air Products and Chemicals, which is the largest — but not the only — commercial supplier, about 9 billion standard cubic feet of hydrogen are delivered each year. Of this, 92% is carried as liquid, 8% as gas, making the total annual liquid delivery near 70,000,000 gallons. There are about 14,000 deliveries and 6,000 fills. Their trucks log about 48,000,000 miles a year. On a given day, there are about 70 trucks on the road.

Liquid hydrogen tank trailers range in capacity from 8 to 16 thousand gallons. These are designed with a double walled vessel with an annular space that operates under a high vacuum. The outer shell may be half an inch thick. The trailers have dual safety valves and dual rupture disk systems to relieve pressure if it builds too high.

The fundamental operational goal is to have no hydrogen loss en route. The vehicles are designed to hold a full load for up to 156 hours before the pressure builds to 13 psig (pounds per square inch as measured on the gauge; i.e., above atmospheric pressure) and venting is required. A full load retains a small gas space in the tank to allow for boil-off. Drivers monitor pressure every two hours. A warning system is visible to the driver when 9 psig is reached. With a partial load, pressures up to 50 psig may be acceptable. Venting, if necessary, is done into a stack that directs the hydrogen away from the ground and nearby ignition sources.

There are also a variety of procedures and equipment to enhance safety during loading and unloading. McHugh in 1980 published the 76 steps involved in delivery. Up to 40 valves have to be operated. Fill lines are purged with helium before transfer. (This helium, which is carried on the truck, also provides a means to extinguish a fire that may occur in a line or in the vent stack.) There are special procedures while loading to ensure a truck is not driven away before it is safe to do so. Operations are outdoors. Vehicles are grounded at two positions. To prevent overfilling, the trucks have liquid level gauges and a full trycock system that can shut down filling operations. Overfilling can cause immediate spillage problems or may require some gas to be vented prematurely. Some facilities use automatic leak detectors, although these are not on the trucks themselves. There is a water deluge system at the loading sites in case of fire. Operators wear NOMEX fire-resistant clothing, including hoods, when appropriate.

All this requires careful training. McHugh in 1980 reported that standard practice at Air Products was for a driver to have about two months of on-the-job training, plus 18 hours in the classroom and 3 hours of video training. There are systematic retraining and review programs.

The safety record of the liquid hydrogen transportation industry is excellent. James Hansel, from Air Products reported the following data. On the road, Air Products has not lost any liquid hydrogen in twenty-five years. There has, of course, been normal venting of gaseous hydrogen. Their overall accident rate is about 1 per 900,000 miles, or about 12 accidents a year. Some of these can be severe. Examples of these include hitting a bridge abutment and shearing the wheels from the trailer, a rollover on to the side, and in one case, a 360 degree rollover. None of these resulted in loss of liquid hydrogen.

The worst recent on-the-road accident occurred when a truck trailer operated by the Linde division of Union Carbide overturned in Columbus, Ohio on August 25, 1987. The truck lost vacuum and the hydrogen boiled off and vented. There was no ignition so there was no significant damage. The potential for fire or explosion, however, led to precautions that did cause considerable disruption: the interstate highway where the accident occurred was closed and nearby homes and businesses were evacuated. [Ref. 15]

Air Products has had five incidents between 1970 and 1993 that occurred because of or coincidental with loading or unloading operations. Some resulted in injuries. (To put this in context, recall there are roughly 6000 fills and 14000 unloadings per year.) Two of these involved purely mechanical problems:

> Hose rupture during loading   (no fire)
> Weld failure on tank while unloading   (small fire)

Three more were related to operating procedures:

> Trailer pull-away with filling hose attached   (no fire)
> Customer station overfill   (small fire)
> Valve leakage   (small fire)

It is interesting to note where the safety issues lie and do not lie. First, of course, the relative infrequency of incidents needs to be emphasized. Clearly the equipment and procedures are designed around hydrogen's basic properties well enough to ensure that hydrogen loss, except for well-controlled venting, is quite rare. Moreover, of the few incidents that have occurred, only one, the weld failure, may have been *initiated* by something associated with a feature unique to hydrogen. The truck rollover and vacuum failure, the hose rupture, and the three procedural problems during loading or unloading could have happened with liquid nitrogen. What is more specific to hydrogen is the subsequent progression of events. Given a release, the race between rapid dispersal and easy ignition depends strongly on circumstances: sometimes the gas ignited and some times it did not. None of the consequences of these incidents were catastrophic, but clearly the potential for explosion colored the response in the Columbus, Ohio incident.

2.2. Factory Mutual Hydrogen Hazard Analysis

Under contract from the Department of Energy in 1977 and 1978, a group from Factory Mutual Research Corporation reviewed hydrogen safety issues and made some comparisons between hydrogen and natural gas. (Zalosh, et al., [Ref. 16]) While not necessarily representing the most current technology and practice, these reports provide an excellent illustration of what can and has happened in handling hydrogen. The issues that arose in this 15 year old study reflect many of the basic

issues concerning leakage, purging, venting, and fire fighting discussed earlier, so it is useful to review this work in some detail.

The stated objectives of the study were

> 1) to conduct a comparative evaluation of the safety records of hydrogen and natural gas;

> 2) to identify hydrogen safety aspects requiring further research or standard/code modification; and

> 3) to quantitatively assess the relative hazards of alternative modes of hydrogen storage, transport, utilization, and disposal.

The first two were addressed. The first did not result in a detailed risk assessment as might be conducted today, although some top-level accident rate and dollar-loss comparisons were developed. The second involved a substantial hazard review. The authors collected incident reports from a wide variety of sources and sought common themes among them.

This hazard analysis nicely complements the transportation experience discussed in Section 2.1. Safety issues in vehicle fuel systems and engine operations may be more like those in industrial processes than anything seen in commercial hydrogen transportation. There are common storage issues. The transportation data developed in this study augments the more current Air Products data discussed earlier.

Data sources

The Factory Mutual group gathered 280 hydrogen incidents reports. Their sources are summarized in Table 3. The major industrial users of hydrogen, as estimated in the report were ammonia production (about 40% of total use in 1974) , petroleum refining (about 40%), and methanol production (about 10%). Since Factory Mutual insured relatively few petroleum refineries, the research team made extra efforts to seek data on refineries from other sources such as the American Petroleum Institute and the Oil Insurance Association. The Nuclear Regulatory Commission data is associated with boiling water reactors where hydrogen gas is created as a byproduct in the cooling loop and must be vented. The Department of Transportation provided Hazardous Material Incident Reports (Department of Transportation Form F 5800.1) involving accidental release of hydrogen during commercial shipment. Most of these, however, were very minor incidents. The "Other" category includes case histories published by the National Fire Protection Association, Manufacturing Chemists Association, The American Institute of Chemical Engineers, and other insurance companies. There were also four incident reports received from 44 requests for data sent by the Factory Mutual team to a variety of ammonia and

methanol manufactures, edible oil hydrogenation plants, iron ore reduction plants, and tungsten and molybdenum processors.

Table 3. Sources of Data for the Factory Mutual Analysis

Source	Number of Reports
Factory Mutual	147
Nuclear Regulatory Commission	40
American Petroleum Institute	31
Department of Transportation	25
British Fire Protection Assoc.	12
Oil Insurance Association	10
Others	15

It proved difficult to assemble relevant data. In some cases, hydrogen-related incidents were contained in much larger data bases. In other cases, the team received limited responses to their requests for data because accident and loss data were seen as confidential or proprietary information. The quality of the incident reports varied. Although 280 incident reports were received, only 173 incidents (145 industrial and 28 transportation) had enough detail to support a hazard analysis. Because the team assembled data from all available sources, it was not clear how representative the data was of the entire population of hydrogen users. This is not a problem when the goal is to identify potential hazards or safety aspects requiring additional consideration, but it was an issue in the comparative evaluation of hydrogen and natural gas.

Hazard analysis for the 145 industrial incidents

Of the 145 industrial incidents, 84 were explosions, 53 were fires, and 8 were either combined fire/explosions or involved unignited vessel ruptures. There were 8 multiple injury accidents. All of these involved explosions. Table 4 summarizes the causes of the incidents. The report gives detailed case histories on one or two incidents of each type. Some salient points are given below. Many of these reinforce the issues raised in Section 1.

In over half the incidents -- those identified in Table 4 as caused by undetected leaks, inadequate purging, plus many in the "Other" category -- *undetected* hydrogen-

reactant mixtures was a factor. In most cases the reactant was oxygen in air, but some of the "Other" incidents involved hydrogen-chlorine reactions.

The "Undetected Leak" incidents typically involved valves, flanges, diaphragms, gaskets, or various seals or fittings. This reflects the ease with which hydrogen leaks. In these cases there was generally no continuous hydrogen monitoring. In one of the incidents described in detail, the fire was underestimated for a considerable period of time because of the nearly invisible hydrogen flame.

Table 4. Causes of 145 Industrial Incidents

Cause	Number of Incidents
Undetected leaks	32
Hydrogen-oxygen off-gas explosions	25
Piping and pressure vessel ruptures	21
Inadequate gas purging	12
Vent and exhaust system incidents	10
Others	45
Total	145

The hydrogen-oxygen off-gas explosions are generally incidents at boiling water reactor power plants. Reactor off-gas venting systems are generally designed to handle low-level explosions, so damage in these cases has been minimal. Personnel exposure to radioactive gasses dispersed in the explosions has been the major concern.

Piping and pressure vessel ruptures were generally the result of materials problems including embrittlement, stress corrosion, and weld failures. In some cases there were nearby ignition sources. In others, there was spontaneous ignition when the vessel burst.

The inadequate gas purging incidents are of considerable concern because detonable mixtures can result. The report gives a case history of an explosion in a hydrogen cooled generator at a coal-fired power plant. When the generator had to be serviced, the cooling system was purged with carbon dioxide. Unfortunately, it

proved very difficult to get all the hydrogen out of this rather complex system. During a welding operation, a low-level explosion occurred.

The vent and exhaust system incidents were either ones where the system was designed to dilute hydrogen below the flammability limit, but did not do so, or ones where air was admitted to what was supposed to be a pure hydrogen vent. The former were typically fan or filter failures; the latter backflow or seal problems. Both illustrate the need for caution when hydrogen venting is needed.

Amongst the others, the largest group were 10 associated with the electrolytic manufacture of chlorine.

Hazard analysis for 28 transportation incidents

Table 5 summarizes the causes for the 28 transportation incidents reported in Ref. 16. (This categorization is the work of this author based loosely on categories used in the NASA data described in Section 2.3; Zalosh, et al. dealt only briefly with these although they published the incident descriptions.) Table 5 also gives the numbers of incidents where the hydrogen ignited. In these outdoors incidents, there are relatively few ignitions and no explosions. This is due in part to rapid dispersal, in part to the lack of ignition sources, and in part to the fact that in many of the incidents, the release was intentional and reasonably well controlled.

Many of the *manual venting* incidents were essentially normal operations: there was pressure buildup in liquid hydrogen tanks because of overfilling, delivery delays, or other causes, and some hydrogen had to be released. The systems are designed for this contingency. The four *vacuum failures* were associated with liquid hydrogen systems. The insulating vacuum on the dewar failed and some cryogenic hydrogen boiled off and needed to be vented. *Transfer leaks* are losses during filling or unloading. In general, very little detail was given on these, so it is hard to know whether these were materials, reliability, or procedural problems. *Rupture disks* are emergency pressure relief features on pressure vessels. In three cases, these relieved prematurely. Two ignited spontaneously, perhaps from static electricity. The cases of valves vibrating open resulted in quite small losses.

The "other" category contains three hard to characterize incidents. In one a chain holding some gas cylinders on a truck failed and in the subsequent fall, one of them ruptured. In another, there was a problem in a vent tube. In a third, the tank trailer detached from the tractor because of an equipment failure. That didn't lead to any release, but there was a problem with the subsequent transfer of gas from the detached tank trailer to another truck and 58,000 cubic feet was lost (without ignition).

Table 5. Causes of 28 Transportation Incidents in FM Database

Cause	Number of incidents	Number of ignitions
Manual Venting	9	0
Vacuum failure w/venting	4	0
On-road accidents	4	2
Leak during transfer	3	2
Rupture disk failure	3	2
Valves vibrate open	2	0
Other	3	2
Total	28	8

On-road accidents were associated with the largest and third largest property losses: $128,000 and $70,000, respectively. The larger of the two, which occurred on September 26, 1972, has the following description: "Car ran stop sign hitting truck; ruptured gasoline tank, piping, inner and outer H_2 tanks; tractor trailer completely destroyed." In the other, dating from October 4, 1971, in South Carolina: "Trailer overturned w/one of ten tubes igniting. H_2 in remaining tubes released later." In each of these incidents, there were two injuries. The other two on-road incidents were more minor. In one, a trailer was hit by a car, but, because of the sturdy construction, there was no release. In the other, a truck went off the road, suffered some damage, and released 2000 cubic feet of gaseous hydrogen without ignition.

Most of these 28 incidents involved liquid hydrogen systems, but 6 of the 8 ignitions were associated with gaseous systems. None of the fires progressed into explosions. Ignitions when rupture disks failed can be associated with the ease with which hydrogen ignites. In most of the other incidents, it is not clear to what extent the damages were increased (or reduced) because of the unique flammability or materials interaction properties of hydrogen.

Hydrogen safety research issues

From this hazard analysis, Zalosh, et al. raise three major research issues. First, further work on leak and flame detection was deemed critical. In 1978, the recommended direction was to look for odorants and flame colorants. This is still an issue, but other means of hydrogen detection have also received attention (Hansel et

al. [Ref. 2]). Second, a better understanding of explosion overpressures, and their dependence on vent areas, enclosure sizes and shapes was seen to be important for future design of venting systems. Vapor cloud explosion overpressure data was also identified as being worth collecting in order to assist in determining the adequacy of existing guidelines for safe separation distances between storage and process facilities. It is interesting to note that since 1978, work on these issues have been published. This work was discussed in Section 1.2 of this report. Finally, in the area of hydrogen ignition, Zalosh recommended developing better emergency venting criteria to avoid spontaneous ignitions.

Hydrogen - natural gas comparisons

The Factory Mutual report made two types of hydrogen-natural gas comparisons. They compared the *dollar loss* attributable to hydrogen and natural gas incidents and they compared the *frequency* of incidents. Database problems were considerable because the quality and representativeness of the data varied widely from source to source. It was necessary to focus on subsets of the data for which comparable natural gas data were available in order to make valid comparisons.

For the dollar loss comparison, the study examined incidents at Factory Mutual insured occupancies. The gross averages suggested the type of fuel made a difference. The median hydrogen and natural gas fire losses were close ($30,000 versus $24,500), but the median hydrogen and natural gas explosion losses were considerably different ($80,000 versus $20,000). The Factory Mutual report presents a reasonably sophisticated statistical analysis that examines whether these differences were primarily a function of gas type or whether other factors more strongly influence the loss data. The factors considered were 1) the deductible value, 2) an inflation index, 3) the type of peril (fire or explosion), 4) the type of gas (hydrogen or natural gas) and 5) the type of occupancy (metal working, boiler rooms, other industrial, non-industrial). Some interactions were also allowed for. The analysis concluded that variation in dollar losses could be explained by the deductible value, the inflation index, and whether the occupancy was a boiler room or not. The latter indirectly represents a hydrogen/natural gas difference since all the boiler rooms were fueled with natural gas. However, the report concludes that, "...there is no statistical evidence to support the hypothesis that hydrogen losses are more severe than natural gas losses." (The underline is in the original report.) It might have been better to add the phrase "in comparable occupancies" to account for the indirect gas relationship with boiler room — non-boiler room occupancies. Also, it would have been interesting to explore whether there were indirect relationships between gas type and deductible value, as would be the case if, for example, hydrogen occupancies tended to have higher deductible values than natural gas occupancies.

For a frequency comparison, it is necessary to normalize the number of incidents to the amount of hydrogen or natural gas consumed. Thus, the authors had to focus on specific industries where both incident and gas utilization data were available. The analysis focused on two such data sets. In both, the incident rate was higher for hydrogen.

The first data set came from the ferrous metal processing industry. Hydrogen is used to reduce iron ore and to prevent oxidation during heat treating. Natural gas is used primarily as a fuel. Factory Mutual insured 43% of the large steel companies at the time of this analysis, so they considered the hydrogen and gas incident rates from their occupancies between 1971-76 to be representative and comparable. In this interval, there were 14 hydrogen incidents and 64 natural gas incidents. On a volume basis, the hydrogen incident rate was 6.4 times higher than the natural gas incident rate (0.289 incidents per billion standard cubic feet for hydrogen versus 0.045 for natural gas). On an energy basis, the hydrogen incident rate was 21 times higher (0.92 incidents per trillion Btu versus 0.043 for natural gas).

The second data set came from American Petroleum Institute (API) reports. Since incident reports are submitted to API on a voluntary basis, the authors considered this data somewhat less reliable. The record may, for example, under-represent some types of common or minor incidents. Hydrogen incident rates were higher, but not as much as was the case in the ferrous metal processing data: 40% higher on a volumetric basis and 4.5 times higher on an energetic basis.

2.3. NASA Hydrogen Safety Experience

Another relatively old review of hydrogen incidents was published by Paul Ordin of NASA in 1974. [Ref. 17]   NASA was one of the first large users of liquid hydrogen. In the Apollo-Saturn program, NASA hauled 16 million gallons of liquid hydrogen, by tanker-trailers and barge. By modern commercial standards, this is not large. At the time it was.

This review describes 96 hydrogen related incidents. While many of the incidents reflect the NASA's unique research and test environment, a top-level categorization of issues presents familiar themes. Of the 96 incidents, 80 involved hydrogen release of one form or another. (The others involved air introduced into the hydrogen system or problems with hydrogen handling equipment that did not lead to release.)   Sixty-six of these were into the atmosphere, with 41 ignitions. This is rather high compared to later experiences.   Twenty of these were into enclosed area; all of these ignited.   (There were six cases of leakage both into the atmosphere and into an enclosed space.)

An effort was also made to identify the specific hardware involved the incidents. About 1/3 of the incidents involved valve malfunctions or leaks (20%) and leaky

connections (16%). Recall that undetected leaks were the largest contributor to the Factory Mutual data. Safety disk failures were an issue in 11% of the incidents. This category was not directly called out in the Factory Mutual analysis. Unsatisfactory materials or embrittlement was a factor in 11% of the incidents. Some of Factory Mutual's piping and pressure vessel ruptures (21% in that database) may be comparable. Another 11% of the NASA incidents were associated with high venting rates. The latter may, in many cases, have been quite specific to NASA operations.

About half of the mishaps were identified as being fundamentally caused by operational or procedural deficiencies. Design or planning problems accounted for most of the rest. Only about 8% of the incidents were out-and-out malfunctions where design and operations were appropriate but some component failed to function as intended. The loading/unloading data from Air Products in Section 2.1 also showed a large fraction of the incidents (3 of 5) being fundamentally procedural problems. The Factory Mutual Analysis in Section 2.2 did not present such a "root-cause" analysis.

About 1/4 of the incidents involved purging problems. This is larger than the fraction one could infer from the Factory Mutual numbers. This too may reflect differences in operations, but it may also include, in part, the different authors varying approaches to categorization.

There were 18 NASA transportation incidents. Table 6 gives the causes, using the same categories as used for the Factory Mutual data. While the categories are loosely based on those given in this NASA report, the categorization was done by the author of this paper from the one or two line incident summaries. This categorization should be reasonably comparable to that for the Factory Mutual data.

No manual venting incidents were recorded in the NASA data, so if we remove these from the Factory Mutual total, the number of incidents in each data base is quite close: 19 versus 18. Although there are some differences, many of the incidents fall into similar categories. With these small numbers, the variation between the NASA and Factory mutual counts is easily explicable by random chance assuming the underlying rates in each category are the same.

In general, the on-road NASA incidents were less severe than those in the Factory Mutual database. In one, a liquid hydrogen trailer overturned and rolled 40 feet down a hill. The tractor was totaled, but there was little damage to the trailer and no hydrogen release. In the second, the tractor trailer jackknifed and turned over. A safety disk ruptured and liquid hydrogen emptied into the roadside mud and snow in about an hour. In the third, the tractor trailer, traveling at 50 miles per hour, was hit by a truck. The trailer was demolished, but there was no hydrogen loss.

Table 6. Causes of 18 NASA Transportation Incidents

Cause	Number of incidents	Number of ignitions	Factory Mutual
Manual Venting			(9/0)
Vacuum failure w/venting	1	0	(4/0)
On-road accidents	3	0	(4/2)
Leak during transfer	6	3*	(3/2)
Rupture disk failure	5	1	(3/2)
Valves vibrate open			(2/0)
Other	3	0	(3/2)
Total	18	4	(28/8)

* One of these led to an explosion.
In one other, consequences of a leak are described as a "burn" to one of
the workmen. This is counted here as an ignition but it may be a cold injury.

2.4. Hydrogen Powered Vehicle Safety Experience

There have been several experimental hydrogen-powered vehicle prototypes in the last twenty years. Many of these were primarily laboratory developments, but a few have seen on-road usage. Below we review this experience.

In the United States, the Los Alamos Scientific Laboratory (now Los Alamos National Laboratory) converted a 1979 Buick Century to use liquid hydrogen. [Stewart, Ref. 18] The project was a joint effort of many parties. The German Aerospace Research Institute (Deutche Forshungs- und Versuchsanstalt für Luft- und Raumfahrt [DFVLR]) supplied the first of two liquid hydrogen storage tanks and collaborated with LASL on the second. Vehicle and engine modifications were sub-contracted to the Billings Energy Corporation. The vehicle was driven a total of 3633 km on hydrogen. The vehicle was refueled 65 times using one of two DFVLR-built semi-automatic liquid hydrogen refueling stations. These were designed for operation by personnel with little or no special training. Most of the problems with this prototype vehicle were associated either with performance or reliability. No major safety incidents were reported, although Stewart does note the hydrogen venting arrangement was not wholly satisfactory. If necessary, hydrogen was vented through a line to the rear of the vehicle. When large amounts needed to be dispersed, a vent stack was attached manually to this line. While no major incidents

were reported, the venting arrangement used "definitely would not be a satisfactory method of hydrogen disposal for a hydrogen-fueled vehicle in public use."

There have been several hydrogen vehicle projects in Germany. DFVLR has fielded liquid-hydrogen vehicles in cooperation with Daimler-Benz AG and with BMW, both before and after their LASL interaction. [Peschka, Ref. 19].

Perhaps the most ambitious project was carried out by Daimler-Benz in the mid 80's. As part of a project sponsored by the German Federal Ministry for Research and Technology, a fleet of five passenger cars and five delivery vans logged more than 200,000 km in Berlin [Ref. 20 and 21]. A central filling station was used and the vehicles were serviced by staff of the Mercedes-Benz Berlin branch. Weight and performance were the major issues in these vehicles, which used hydride storage. Neither report identifies any particular safety incidents. There were some operational constraints. Povel, et al. [Ref. 20] notes, without detail, that there were regulations for parking vehicles in enclosed spaces and that "ventilation of the passenger compartment and storage system prevents undesirable hydrogen concentration if there is a leak." None-the-less, Feucht, et al. [Ref. 21] notes, "Above all, no safety-relevant malfunctions occurred in the hydrogen systems of the vehicles."

There have been other vehicle prototypes, but this author has seen no others with significant on-road exposure. For example Watson, et al. [Ref. 22] reports on an Australian vehicle that was primarily a technology test-bed. Although it was registered for road use and performed acceptably there, most testing was done in the laboratory.

Peschka [Ref. 19] reports on three accidents involving hydrogen powered vehicles, none very serious. In 1975 a UCLA AMC Jeep was being towed and the trailer tipped over. It came to rest up-side down. This caused liquid hydrogen to come into contact with the relatively warm top of the storage vessel. The vessel was not designed for that contingency and there was a rapid boil-off of liquid hydrogen. Hydrogen was manually vented without incident, the car was righted, hydrogen was vented again, and the vehicle was driven back to UCLA on hydrogen. There was no damage to the hydrogen system, but the vehicle did sustain some body damage.

In 1982, during the fourth World Hydrogen Energy Conference, a liquid hydrogen DFVLR BMW-520 was involved in a minor collision in Pasadena. The BMW, stopped at a traffic light, was hit by a limousine and pushed about 7m into an intersection. There was damage to the car body, the fuel lines were bent a bit, and the drive shaft tunnel had some cracks, but there was no hydrogen leak.

This same BMW-520 suffered a towing accident much like the 1985 Jeep incident in Bonn in 1984. There was body damage, but no damage to the liquid hydrogen tank or fuel system.

This experience is, of course, quite limited, so one must be careful about drawing conclusions. There is no evidence of gross safety problems, but given the very limited experience, less frequently occurring problems may not have surfaced. It is worth noting that minor compromises in convenience have been made in the name of safety.

3. Safety Issues for Hydrogen Vehicles Development

We can now return to the question raised at the beginning of the report: "What system design and operational features must be in place (and at what cost in money and convenience) to assure that hydrogen-powered vehicles will be safe?" As noted in the introduction, it is premature to prescribe specific features or design choices is premature, but we can discuss the some issues that these will have to address. Based on the physical properties and first order principles and operational experiences with hydrogen discussed earlier in this report, Section 3.1 reviews design issues as they apply in normal operations, in maintenance and fueling, and in abnormal circumstances. This paper is, of course, limited in its scope. Section 3.2 discusses on-going safety analysis for vehicle development.

3.1 Design Issues

Several issues must be considered for the safe design and operation of hydrogen powered vehicles. Clearly many of the themes that appear in hazard studies drawn from other applications -- preventing leakage, completely purging air from all hydrogen carrying lines and purging hydrogen afterwards, operating outdoors whenever possible, and allowing for safe venting -- apply here. Some other areas of safe vehicle operation have been explored in the literature, notably in Hansel, et al. [Ref. 2].

During normal operation, the two concerns are unintentional leakage of the fuel system and managing venting safely. Regarding leakage, it is worth noting that even with gasoline engines, more than half of vehicle fires are not collision related. Fuel system problems account for about a third of all vehicle fires [Karim, Ref. 4]. Thus, hydrogen leak prevention and detection appear to be critically important. As noted in Section 2, leakage and storage and piping failure have proven historically to be the largest sources of hydrogen handling problems. And also as noted earlier, this is largely a matter of good engineering. Materials must be selected appropriately and metal-to-metal joints and packless valves are preferred. [Ref. 2]

Leak detection is not unique to hydrogen. Draft NFPA Standard 57 for Liquefied Natural Gas Vehicles [Ref. 23] calls for continuous leak detection if the gas is not odorized, as hydrogen used for fuel cells may not be, and if the fuel is stored in the interior of the vehicle.

Venting is especially an issue for vehicles with liquid hydrogen storage where boil-off is unavoidable, but it is at least a background issue for any system utilizing pressured hydrogen. Safe venting was identified as an issue in the LASL test vehicle over a decade ago. Venting issues appeared in the Factory Mutual and NASA studies earlier than that. The current state of the art is to have about 1.8% boil-off per day. In many applications, this means venting of hydrogen would be required in about a week if the vehicle is not driven. To avoid flammable or detonable fuel-air mixtures, venting cannot be done into a confined, unventilated area. This either puts limitations on parking a vehicle in a garage for an extended period, requires careful external venting, or requires some sort of internal gas capture. For an example of the latter, Peschka [Ref. 19] suggests excess hydrogen might be used in a small fuel cell to charge the battery. Catalytic combustion has also been suggested. Vents should be positioned upwards, both to capitalize on hydrogen's buoyancy and rapid dispersal and to avoid ignition sources, which, out of doors, are primarily at ground level.

Refueling raises additional safety concerns. During refueling, vehicles should be well grounded. Hansel [Ref. 2] suggests the possibility of a metal whisker system that automatically grounds a vehicle drive into refueling positions. As in all other applications, care is needed to keep air out of hydrogen tanks and filling lines. The refueling station must be prepared to deal with hose and line ruptures, caused by equipment failure or operator mistakes such as driving away before disconnecting the lines. Excess flow shutoff valves and break away fittings are two obvious mechanical ways to enhance safety in such instances, but means to ensure observance of safe operating procedures are equally important. The latter is emphasized by the observations in several of the hazard analyses that procedural problems are often at the root of hydrogen handling incidents. At the same time, refueling procedures need to be reasonably simple for general acceptance. Operations and storage tanks should be outdoors to maximize dispersal in event of a spill if at all possible. If not, good ventilation above storage or fueling areas is critical. Periodic leak detection of major filling station elements will be useful. Continuous hydrogen detection, which still needs technology development, might also enhance safety in indoor operations.

Vehicle maintenance, too, raises issues. As noted, purging hydrogen from a complex piece of equipment may prove difficult. Maintenance should be done outdoors or in very well ventilated areas and ignition sources in the entire area need to be carefully controlled. As was true with refueling stations, careful adherence to

safe operating procedures may be the most important feature of a safe maintenance shop.

Finally, any design must consider abnormal circumstances. There are obvious weight trades between crashworthiness and performance and some well-considered design work will be needed. Reasonable, if somewhat general, guidance is to keep the fuel tank away from the sides of the vehicle and protect the outlet plumbing. Further, it has been suggested that storage and piping of lighter-than-air fuels such as hydrogen or methane be near the top of vehicle so that in case of a leak or breach. This obviously has to be reconciled with the desire to protect the fuel system in a crash or rollover. Storage vessels may prove more robust than the lines in the vehicle's fuel delivery system. If this is the case, automatic excess flow shutoff valves on the storage vessel may be desirable. The draft natural gas powered vehicle standard requires the fuel tank and attached valves and other items attached there to be able to withstand 8 g's. [Ref. 23] An earlier 1992 draft, reported in Hansel et al. [Ref. 2], required shock loadings between 27 and 60 g's. Liquid hydrogen systems have to provide for safe emergency venting in the case of vacuum failure or a fire heating the dewar. The UCLA Jeep experience emphasizes the importance for designing a storage system that is safe in any orientation. Compressed systems need pressure let down systems, check valves, and relief devices to handle regulator failures. Hydride systems may have an advantage here since there is considerably less free hydrogen gas available in the system.

3.2. Follow-on Safety Studies

This paper surveyed the published literature regarding hydrogen vehicle safety. There are several areas that need follow-up. First, the emphasis here has been more on hydrogen safety than on vehicular safety. Perhaps the best next step in developing a picture of hydrogen vehicle safety would be to explore the vehicular safety aspects further. Natural gas vehicle experience is considerable and presents some of the same safety issues as does hydrogen. Gasoline vehicles are, of course, the standard, and the safety experience and literature there is considerable.

Second, the records of both the nascent hydrogen vehicle industry and the hydrogen transportation industry could be filled out beyond what has been done here. Some of this data is available from scattered sources. Obtaining additional vehicle information would require international cooperation since much of the recent prototype development has been outside the United States. Obtaining further transportation safety information would require cooperation from the major hydrogen suppliers, Air Products, PraxAir (formerly the Linde division of Union Carbide), and Airco, as well as the Department of Transportation and industrial safety organizations such as NFPA.

After more of the background data is developed, a structured risk analysis of hydrogen vehicle safety is certainly feasible using modern event and fault tree tools. An event tree identifies the potential failure and accident sequences by systematically organizing 1) the locations where a hydrogen vehicle could experience an incident, 2) the event that could initiate an incident, and 3) the subsequent series of events that identify system response, perils involved, and the consequences incurred. To each branch we can, in theory, attach a probability, but simply enumerating the branches is often a useful step. Steps 1) and 2) for hydrogen vehicle incidents may not be all that much different for a gasoline vehicle, although the importance of various branches may be quite different. The latter step might be quite different, although there may be some commonalty here with natural gas powered vehicles. Folding in the components and component responses unique to a hydrogen fuel system would then provide a tool to guide where resources must be directed to produce a demonstrably safe hydrogen vehicle.

The safety standards to which hydrogen-powered vehicles will be held can only be conjectured at this time. Unfamiliar technologies are often held to higher standards than their in-use predecessors. From today's perspective, this issue looms large: gasoline vehicles are the norm and hydrogen safety is publicly associated more with one spectacular incident a half-century ago than with the outstanding commercial hydrogen transportation record in the last decades. The perspective in the future may be more moderate. The increasing use of natural gas powered vehicles will do much to mitigate the unfamiliarity-bred concerns about gaseous transportation fuels. Well-managed fleets of hydrogen-powered busses or commercial vehicles may make hydrogen more familiar. While real technological, economic, and operational issues remain, the requirements for very low or zero emissions combined with the eventual need to supplement fossil fuels make the concept of hydrogen-powered vehicles attractive. Good design and appropriate operations can make them safe.

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